Glass and Ceramics, Vol. 69, Nos. 5 – 6, September, 2012 (Russian Original, Nos. 5 – 6, May – June, 2012)

SCIENCE FOR CERAMIC PRODUCTION

UDC 666.3:535.345

ADVANCED OPTICALLY TRANSPARENT COMPOSITE CERAMIC MATERIALS

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Translated from *Steklo i Keramika*, No. 5, pp. 46 – 48, May, 2012.

The factors affecting the process of obtaining transparent ceramic materials are analyzed. Methods for obtaining materials based on yttrium oxide and yttrium-aluminum garnet, transparent in the visible region of the spectrum, are shown. The heat-treatment regimes for materials in air and in vacuum are established. The mechanisms for creating composite transparent material combining the properties of its constituent oxides are developed. A material with high heat-resistance, thermal conductivity and light transmission in the visible region of the spectrum is obtained.

Key words: transparent ceramic, yttrium oxide, yttrium-aluminum garnet, scandium oxide, composite material, solid-state laser.

Materials based on yttrium oxide and yttrium-aluminum garnet (YAG) have high light transmission in the visible region of the spectrum. Such ceramic can replace glass in devices operating under night vision conditions, at high temperatures, in aggressive media and so forth [1]. Relatively recently cerium-activated luminophores with garnet structure started to be used for white-light LEDs (US Patent 6744196). The introduction into ceramic of activator ions Nd^{3+} (WO patent 02/42828), Cr^{3+} (US Patent 6859480), Er^{3+} and Yb^{3+} [2] makes it possible to use the ceramic as the active materials of a solid-state laser.

The methods for producing blanks based on yttrium oxide and yttrium-aluminum garnet are diverse: semidry pressing, hot casting under pressure, colloidal casting, hot and hot isostatic pressing [3]. As a rule, such ceramic is annealed in vacuum or a hydrogen medium. However, without introducing modifying additives ThO_2, HfO_2 and others it is practically impossible to sinter yttrium oxide ceramic to a dense state by methods that do not require the application of external actions [4].

Such additives and special methods for obtaining transparent materials are used due to increasing production costs of the final product. In addition, the presence of tetravalent cations impedes the use of such ceramic in laser technology [5]. To obtain an active body based on yttrium-aluminum garnet, aside from the activator ion, the modifying additive scandium oxide is introduced, which makes it possible to obtain material with high light transmission [4].

Thus, good prospects now exist for developing new composite materials which do not contain tetravalent modifier ions and combine the relatively low cost and simplicity of obtaining materials based on yttrium oxide as well as the optical and laser properties of materials made from YAG.

Methods for synthesizing the initial yttrium oxide and yttrium-aluminum garnet powders are diverse [4]. The first one can be obtained using the sol-gel technology by thermal decomposition of salts; the second one uses solid-phase synthesis and “combustion,” “freezing out,” co-precipitation, sol-gel and hydrothermal methods.

Analysis of methods for synthesizing yttrium oxide and yttrium-aluminum garnet shows that most methods are applicable only under laboratory conditions.

The most practicable method is co-precipitation [5]; it is easy to implement, gives excellent reproducibility and makes it possible to obtain powders whose particles (100 – 500 μm) are bound into loose, easily destroyed aggregates no larger than 10 μm. This method makes it possible to vary the technological parameters over a wide interval and ultimately to

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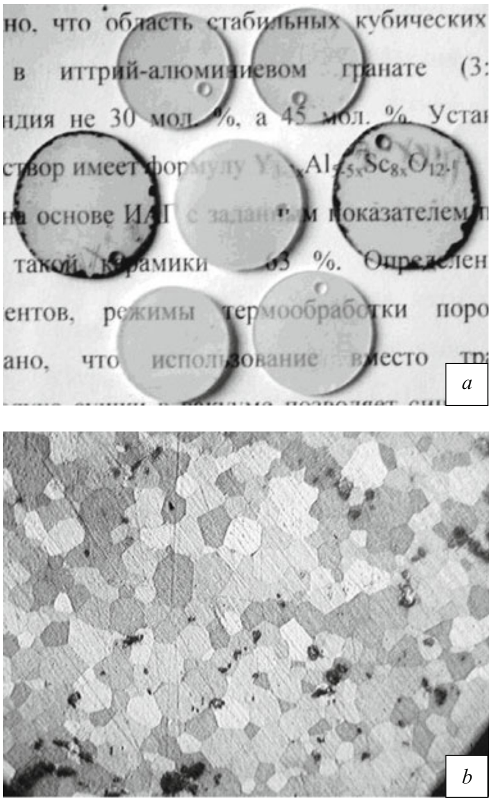

Fig. 1. Exterior view of the samples: *a*) ceramic based on YAG (top row); ceramic based on yttrium oxide (middle row at the ends); composite ceramic based on yttrium-aluminum garnet and yttrium oxide (middle row at the center and bottom row); *b*) microstructure of the composite transparent ceramic: thermal etching (×700).

change the size and structure of the particles and the particle-size composition of the powder.

In the present work, yttrium oxide obtained by thermal decomposition of yttrium carbonate was used as the matrix to obtain a composite transparent material, while yttrium-aluminum garnet synthesized by thermal decomposition of a stoichiometric mixture of yttrium and aluminum hydroxides was used as the filler. Petrographic and electron-microscopic analysis showed that the powders obtained consist of isometric particles 1 – 7 μm in size. X-ray phase analysis showed that the powders are x-ray amorphous, which also confirms that their dispersity is high.

After heat treatment yttrium oxide and yttrium-aluminum garnet were studied by electron microscopy. Spherical particles of yttrium oxide to 500 nm in size were united into loose isometric aggregates to 3 μm in size. Prismatic YAG particles to 1 μm in size were united into aggregates to 5 μm in size. IR spectroscopy of the initial mixture of hydroxides and the powder obtained after roasting showed that characteristic bonds of yttrium-aluminum garnet are present already at the co-precipitation stage.

The yttrium oxide and yttrium-aluminum garnet powders obtained were mixed in the ratio 1 – 70 wt.%. These powders were used to press 30 mm in diameter, 3 mm high disks. The disks were annealed in air at temperatures 1000 – 1500°C with soaking at the final temperature for 2 – 4 h and then in vacuum at 1600 – 1890°C for 1 – 10 h.

Properties of the Optically Transparent Composite Ceramic Obtained

Light transmission at λ = 700 nm, %	70
Dielectric constant (10^6 Hz)	11.8
Tangent of angle of dielectric losses	1×10^{-4}
Heat-resistance (1200°C – air thermal cycles)	28 – 30 cycles to fracture
Thermal conductivity, W/(m · K)	9
Ultimate bending strength, MPa	300

This ceramic combines the high electrophysical and optical properties of yttrium oxide and the thermophysical and mechanical properties of YAG. Even though it possesses light transmission 70%, because of the properties which are combined in it this material can be used in laser technology, specifically, in disk lasers with semiconductor diode pumping. An exterior view of the samples is presented in Fig. 1.

The next stage of the work was to evaluate the possibility of using the new materials as the active medium in a solid-state laser. Lasers are most widely used in medical, computer and military technology. As a rule, these are Nd^{3+}-activated pulsed blue, green or violet lasers and Eu^{3+}-activated red lasers.

This aspect dictated the choice of the activator ions used in this work. Chemically pure-grade rare-earth metal salts – neodymium and europium nitrate were used as the initial components.

The technology described in detail above was used to obtain ceramic with additions of activator ions. The molar content of REM oxide additives was less than 1%. After heat-treatment the material with neodymium oxide as the additive has a violet color while the material with europium oxide is orange.

Petgrographic studies showed that in both cases the material is practically pore-free; the intercrystalline porosity does not exceed 1%. The crystals are mainly isometric in shape; the average size of the crystals is 2 μm. It should be noted that as a result of the introduction of rare-earth metals as additives the crystals are smaller than in the case of the unactivated ceramic. Coalescence of crystals and formation of coherent boundaries are also observed; it was assumed previously that the reorientation of the crystals to geometric coincidence is possible only for ceramic with a large-crystal structure.

The light-transmission spectra of the activated ceramic are displayed in Fig. 2.

Analyzing the spectra, it can be concluded that the activator ions in a polycrystalline matrix are in a trivalent state, while the absorption bands clearly seen in the spectrum cor-

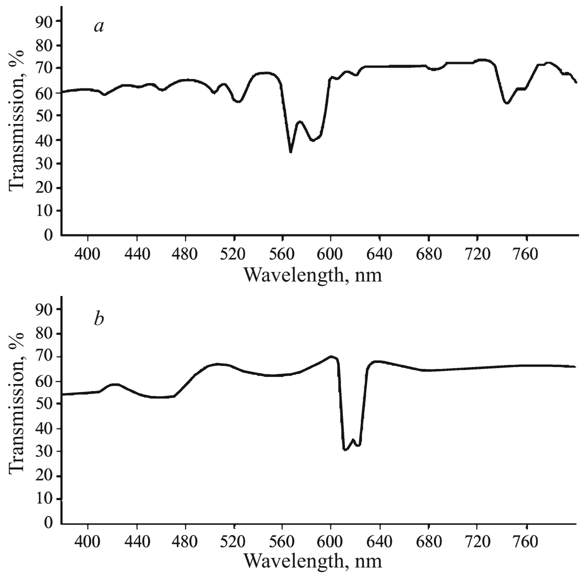

Fig. 2. Light-transmission spectra of ceramic: *a*) Nd^{3+} activated; *b*) Eu^{3+} activated.

respond to wavelengths preferably used to pump the indicated activator ions.

In summary, the technology developed for preparing powders and ceramics based on them can be used to obtain new transparent materials meeting the requirements for the active media of solid-state lasers.

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